THERMAL DECOMPOSITION OF CALCIUM SUPEROXIDE

A. B. Tsentsiper and R. P. Vasil'yeva

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546   AUGUST 1974

1. Report No. NASA TT F-15,873	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle THERMAL DECOMPOSITION OF CALCIUM SUPEROXIDE		5. Report Date AUGUST 1974
		6. Performing Organization Code
7. Author(s) A. B. Tsentsiper and R. P. Vasil'yeva		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address Techtran Corporation P.O. Box 792 Glen Burnie, Maryland 21061		11. Contract or Grant No. NASw-2485
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION WASHINGTON, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

A study has been made of the kinetics of decomposition of calcium superoxide prepared by vacuum decomposition of the compound $CaO_2 \cdot 2H_2O_2$. An activation energy for the process equal to 44 kcal/mole has been found. Moreover, there is initially a rise in the superoxide/peroxide ratio (samples of the superoxide are never pure, and usually contain 50% or less of the superoxide); this rise is attributed to a continuation of the same type of reaction as that involved in the initial preparation, a further oxidation of the peroxide by hydrogen peroxide still present. Later, a decomposition of the superoxide sets in; this is stated to proceed directly to the oxide. This type of reaction is explained by the supposition that the peroxide is a labile intermediate in the decomposition, and this explanation is given support by the fact that the decomposition temperature of the peroxide is not greatly above that of the superoxide.

17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified-Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 5	22. Price

-ii-

THERMAL DECOMPOSITION OF CALCIUM SUPEROXIDE

A. B. Tsentsiper and R. P. Vasil'yeva[1]

The existence of $Ca(O_2)_2$ was first indicated in the work of [1]. Much /1380* research on finding the conditions most favorable for the formation of $Ca(O_2)_2$ have led to preparation of a sample by decomposition of $CaO_2 \cdot 2H_2O_2$ under vacuum; in this the superoxide content reached 50% [2]. Preparations with an admixture of $Ca(O_2)_2$ are paramagnetic, and their magnetic susceptibility rises with increase in superoxide [3]: in the work of [4] it was demonstrated that the paramagnetism of these preparations is caused by the O_2^- ion. A decomposition temperature of 290° has been established for $Ca(O_2)_2$ on the basis of thermographic curves [3]. It has been suggested that the decomposition takes place to CaO_2, which further loses active oxygen at 340°. We have indicated that the preparation obtained by decomposition of $CaO_2 \cdot 2H_2O_2$ under vacuum is not homogeneous, but consists of an x-ray-amorphous phase which contains mainly $Ca(O_2)_2$ plus crystalline $Ca(OH)_2$ [5].

Experimental

The starting sample was prepared by decomposition of $CaO_2 \cdot 2H_2O_2$ in vacuum at 50° [6]. Decomposition of the $Ca(O_2)_2$ was carried out under static conditions in the set-up described in [7]. Pressure changes was registered on a differential manometer. At the end of an experiment, the preparation was analyzed for O_2^{2-} and O_2^- content by the procedure of [3]. In Figure 1 we show the dependence of the rates of oxygen evolution in mm Hg pressure per minute, referred to 1 g of starting sample, on time in the decomposition of a preparation containing 32% $Ca(O_2)_2$. It was shown that the change in superoxide content is only somewhat reflected in the rate of the process: the rate curves at all temperatures and for various compositions are characterized by an induction period and by a maximum. It is evident from the table that a certain time after the start of the experiment (first sample) the content of O_2^- rises approximately

---

*Numbers in the margin indicate pagination in the foreign text.

1

as much as that of O_2^{2-} decreases; the O_2^-/O_2^{2-} ratio rises. If one considers that evolution of oxygen is not taking place during this period, it may be suggested that the following reaction is taking place

$$2CaO_2 + H_2O_2 \text{ bound} \rightarrow Ca(O_2)_2 + Ca(OH)_2.$$
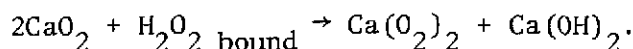
BASIC DATA ON THERMAL DECOMPOSITION OF PREPARATIONS
CONTAINING $Ca(O_2)_2$

| T, °C	Time, min	Composition of first sample, %			Time, min	Composition of second sample, %		
		O_2^{2-}	O_2^-	O_2^-/O_2^{2-}		O_2^{2-}	O_2^-	O_2^-/O_2^{2-}
Starting figures: O_2^{2-} 10,5%, O_2^- 9,8%, O_2^-/O_2^{2-} = 0,9								
250	80	7,4	13,5	1,8	250	4,4	8,3	1,9
260	50	7,3	13,3	1,8	180	4,6	7,6	1,7
270	25	7,4	13,6	1,8	120	3,0	4,6	1,5
280	—	—	—	—	150	1,9	3,6	2,0
Starting figures: O_2^{2-} 10,8%, O_2^- 6,5%, O_2^-/O_2^{2-} = 0,6								
200	200	8,0	11,0	1,4	—	—	—	—
250	120	8,2	10,0	1,2	160	7,0	9,2	1,3
270	30	7,7	9,0	1,2	120	5,5	4,7	0,9
280	12	7,5	10,9	1,4	60	4,4	5,7	1,3

Commas indicate decimal points.
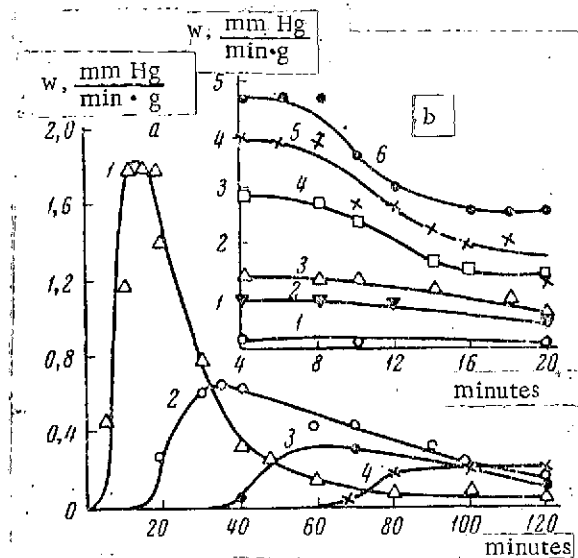
Figure 1. Change in Rate of Decomposition with Time. a) $Ca(O_2)_2$: 1) 280°; 2) 270°; 3) 260°; 4) 250°. b) CaO_2: 1) 310°; 2) 320°; 3) 330°; 4) 340°; 5) 350°; 6) 360°.

Probably a slight amount of H_2O_2 is retained after the decomposition of $CaO_2 \cdot 2H_2O_2$ at 50° because of strong hydrogen bonding, and this reacts with CaO_2 only at higher temperatures. In the active stage of the process, when evolution of oxygen begins, the O_2^-/O_2^{2-} ratio essentially does not change. Apparently the $Ca(O_2)_2$ decomposes not to the peroxide, as the authors of [3] have suggested and as is the case in the decomposition of NaO_2 [7], but to the oxide. This is the more probable, since decomposition of $Ca(O_2)_2$ takes place at

2

temperatures which are comparatively close to the decomposition temperature of CaO_2, as is evident from Figure 1, b, where we show the rates of oxygen evolution in decomposition of CaO_2 containing 18.3% O_2^{2-}. The degrees of conversion of the O_2^{2-} at the end of the experiments were 52, 41, 35, 24, 18, and 7%, respectively, at 360, 350, 340, 330, 320, and 310°. The character of the kinetic curves and the activation energy of 44 kcal/mole essentially agree with the figures obtained in [8]. Although the decomposition of CaO_2 takes place at higher temperatures than that of $Ca(O_2)_2$, it may be assumed that the peroxide which is formed in a labile state, is unstable already at the decomposition temperature of $Ca(O_2)_2$. An apparent activation energy for the decomposition temperature of $Ca(O_2)_2$ of 45 kcal/mole was determined from the log w_{max} versus 1/T dependence. S. D. Kaitmazov has taken the paramagnetic resonance spectrum of preparations at various stages of decomposition. The spectrum lines which are slightly asymmetric with a small anisotropic broadening indicate the presence of O_2^-. The concentration of the ions proved approximately two orders of magnitude less than the concentration of $Ca(O_2)_2$ as determined analytically, which is apparently connected with a spin-spin interaction which leads to considerable line broadening. Although the relationships considered above were obtained in decomposition of a preparation containing 32% $Ca(O_2)_2$, we assume that they may be attributed to the decomposition of practically pure superoxide. As a matter of fact, that initial preparation by the procedure of [5] is a mixture of two phases, one of which consists mainly of $Ca(O_2)_2$ and evidently determines the kinetics of the process. The second $Ca(OH)_2$ phase is an inert admixture in this process; the fact that a change in composition of the starting preparation hardly shows up in the kinetics of the process serves as support for this view.

Conclusions

1. A marked decomposition of $Ca(O_2)_2$ in the preparation obtained on decomposition of $CaO_2 \cdot 2H_2O_2$ under vacuum takes place above 250°. The rates pass through a maximum, E = 45 kcal/mole.

2. At the beginning of the decomposition, an increase in O_2^- content is observed, plus a corresponding loss of O_2^{2-}; this is apparently connected with the reaction $2CaO_2 + H_2O_2 \rightarrow Ca(O_2)_2 + Ca(OH)_2$, where the H_2O_2 is perhydrate

hydrogen peroxide of crystallization remaining after the decomposition. In the active stage of the process, a decomposition of the $Ca(O_2)_2$ to the oxide takes place.

REFERENCES

1. Iraube, W. and W. Schulze, *Ber.*, Vol. 54, p. 1626, 1921.
2. Vol'nov, I. I. and A. N. Shatunina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, p. 2031, 1966.
3. Vol'nov, I. I., V. N. Chamova, V. P. Sergeyeva and E. I. Latysheva, *Zh. Neorgan. Khimii*, Vol. 1, p. 1937, 1956.
4. Johnston, R. S., *Analyt. Chem.*, Vol. 30, p. 511, 1958.
5. Bakulina, V. M. and A. B. Tsentsiper, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1968.
6. Vol'nov, I. I. and V. N. Chamova, *Zh. Neorgan. Khimii*, p. 522, 1960.
7. Tsentsiper, A. B. and S. A. Tokareva, *Ibid*, Vol. 1, p. 2474, 1961.
8. Averbukh, B. D. and G. I. Chufarov, *Zh. Obshch. Khim.*, Vol. 21, p. 629, 1951.